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Thermal characterization and pyrolysis kinetics of tropical biomass feedstocks for energy recovery

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ABSTRACT

This paper aims to analyse energy related properties, thermal degradation behaviour and devolatilization kinetics of five Cameroonian biomasses namely, Palm Kernel Shells (PKS), Mesocarp Fibres (PMF), Coffee Husk (CH), Corn Cob (CC) and Peanut Shell (PNS). The thermal degradation was performed using thermogravimetric analysis (TG). Different behaviours related to the presence of chemical constituents such as cellulose, hemicellulose and lignin were obtained. Comparison of the thermal characterization shows that PMF is the most interesting feedstock with the highest heating values and reactivity due to higher volatile content. Decomposition of TG data was analysed by applying diffusion and chemical reaction kinetic models. Obtained results show that biomass pyrolysis is represented by two successive steps. The devolatilization stage characterized by high weight loss rate is well described by diffusion reaction models. In contrast, the char formation stage characterized by low weight loss rate is well described by third order chemical reaction models.

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Introduction

The utilization of renewable energy sources is currently crucial to reach the changes required to reduce the increasing global warming impacts. Biomass represents a promising renewable energy with a large potential to substitute fossil fuels (McKendry, 2002a).

Biomass energy is widely used in the third world principally in rural regions where it is frequently the main energy source for cooking. Although the agricultural waste potential in many of these regions, few attentions are given to them.

Cameroon is a country in Middle Africa with about 20.03 million people (2011 census) and 50% of its population are below the national poverty line. Cameroon has the third major biomass potential in sub-Saharan Africa, with amount estimated at 6.3 billion tons (Ackom et al., 2013). Forest resources cover about 28 million ha and represent the three-quarters of the country's territory (Maesano et al., 2013). Wood fuel is the main energy source for cooking in both rural and urban Cameroonian areas. However, the unsustainable use of this resource (e.g. wood extraction-commercial, charcoal production and fuel wood) has led to important deforestation throughout the country (Mbatu, 2010).

This deforestation has encouraged research to identify and to use other biomass resources as a viable substitute of fuel wood. Since Cameroonian agriculture contributes to a great degree to the country's GDP, these generated residues may represent a promising alternative fuel (Ackom et al., 2013).

Soils and climate on the country's coast promote farming of oil palms, bananas and cocoa. The South Cameroon Plateau interior encourages cultivation of cash crops such as coffee, tobacco and sugar. Major agricultural produce in northern country includes cotton, corn, peanuts and rice.

These crops' cultivation as well as their transformation through agro-industrial processes generate in Cameroon a significant amount of residues. Hence, the palm oil extraction in the traditional mills mainly generates Palm Kernel Shells (PKS) and Mesocarp Fibres (PMF). Additionally, the coffee industry induces important amounts of Coffee Husk (CH) before the roasting coffee process. Furthermore, the maize and groundnut productions left certain amounts of Corn Cobs (CC) and Peanut shells (PNS). These valuable residues are usually cheap, widespread, and continuously produced. All these renewable energy resources have the potential to be widely used as source of energy both by the local populations (e.g., cooking and heating) and for industrial energy consumption.

In order to efficiently use them for energy production, various thermochemical conversion processes such as carbonization, combustion, gasification and liquefaction have been developed (McKendry, 2002b). However, these procedures involve pyrolysis because it is the primarily stage of biomass transformation (Yaman, 2004).

Kinetic studies of pyrolysis are usually conducted using a thermogravimetric analyser (Chouchene et al., 2012; Dorge et al., 2011; El may et al., 2012; Jeguirim et al., 2010; Jeong et al., 2014; Masnadi et al., 2014). The kinetic parameters include the activation energy, the

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frequency factor and the kinetic rate constant K. These parameters are required for the reactor designing since it is necessary to achieve an optimal conversion. Their usefulness with respect to modelling their respective thermochemical conversion processes is acknowledged. In fact, the data obtained from the thermal analysis are provided to kinetic models which use rate laws that follow the fundamental Arrhenius rate expression.

The main purpose of this investigation is to study the thermal characterization and the devolatilization kinetics of five Cameroonian biomass feedstocks: Palm Kernel Shells (PKS), Palm Mesocarp Fibres (PMF), Coffee Husk (CH), Corn Cobs (CC) and Peanut Shells (PNS) using thermogravimetric analysis data and the Coats and Redfern method. Comparison of thermal characteristics of the different biomasses is performed to assess the eventual utilization of the different biomasses for energy recovery.

Materials and methods

Raw materials

Five types of Cameroonian biomass were studied: Palm Kernel Shells (PKS), Mesocarp Fibres (PMF), Coffee Husk (CH), Corn Cobs (CC) and Peanut Shells (PNS). PKS and PMF were obtained from the SOCAPALM palm oil mill in Douala. CC samples were provided by MAISCAM agro-industrial company in Ngaoundéré. PNS were provided from a farmer cooperative from the region of Garoua. CH samples were supplied by a farmer cooperative in Nkongsamba. All of these samples were dried naturally to reduce their moisture contents. Therefore, the samples were crushed and sieved into 1–2 mm particle size. The obtained samples were stored in a glass jar at room temperature.

Proximate and elemental composition

The design of an operating plant for biomass thermochemical (pyrolysis, gasifier and combustor reactors) requires the composition analysis of the fuel as well as its related energy properties. Hence, elemental compositions of the different biomass species were performed by a CHONS-NA 2100 protein CE Instruments analyser.

Proximate composition was obtained using a thermogravimetric analyser (METTLER TOLEDO 851) using the TG procedure analysis. This method is given in details in previous investigations (El may et al., 2012).

The energy contents of the different samples were obtained using an IKA adiabatic oxygen bomb calorimeter by determining the high heating values (HHV). The low heating values (LHV) were calculated using the relationship between HHV and LHV given by:

$$\mathrm{LHV} = \mathrm{HHV}–\mathrm{hg}(9\mathrm{H} + \mathrm{M})/100$$

where H and M are respectively the hydrogen percentage and the moisture percentage of the received tested fuel. Here, hg is the latent heat of steam in the same units as HHV and LHV.

Thermogravimetric analysis

Thermal degradation behaviour of biomass species was frequently investigated using thermogravimetric analyses. In this present study, a thermobalance (METTLER TOLEDO 851) was used. Before each experiment, sample with weight about 10 mg was put in an alumina crucible (diameter 4.5 and height 7 mm). TGA experiments were performed under a gas flow of 12 NL/h at heating rates of 5 $\mathrm{K \cdot min^{-1}}$ from room temperature to 900 °C.

Theoretical approach

In this present study, the Coats–Redfern model was used for determining the kinetic parameters of the thermal degradation of the different samples (Coats and Redfern, 1964, 1965). Hence, various kinetic models adapted for the biomass decomposition (Table 1) were applied to analyse TG and DTG data. In fact, previous investigations showed that the biomass degradation process is governed by transport (diffusion) phenomena and chemical reactions (Gil et al., 2010; Guo and Lua, 2000; Masnadi et al., 2014; Park and Jang, 2012; Vlaev et al., 2003; Yorulmaz and Atimtay, 2010).

The reaction scheme (1) may describe the pyrolysis process (Brown, 2001):

$$\mathrm{B_{solid}} \rightarrow \mathrm{C_{solid}} + \mathrm{D_{gas}} \tag{1}$$

where $\mathrm{B_{solid}}$ is the initial biomass, and $\mathrm{C_{solid}}$ and $\mathrm{D_{gas}}$ are the different products during the degradation of $\mathrm{B_{solid}}$.

A typical model for a kinetic process can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $f(\alpha)$ is a function which depends on the reaction mechanism, $k(T)$ the rate constant; T the absolute temperature, t the time and $\alpha = (\mathrm{w} - \mathrm{w_f})/(\mathrm{w_0} - \mathrm{w}_f)$ the degree of the reaction transformation of the sample (w is the mass at any time and subscripts 0 and f respectively refer to the initial and final masses).

The temperature dependence of the rate constant is described by the Arrhenius equation:

$$\mathrm{k} = A \cdot \ \exp\left(-E/RT\right) \tag{3}$$

where A is pre-exponential factor, E the activation energy and R the universal gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$). Under constant heating rate:

$$\beta = \frac{dT}{dt} = cte \tag{4}$$

and after replacement in Eq. (2) and some changes

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} \exp\left(-\frac{E}{RT}\right)dT. \tag{5}$$

The right hand side of Eq. (5) has no exact analytical solution, but production of some variable switches and applying Cauchy's rule the

Table 1
Algebraic expressions of functions used for biomass thermal degradation.

Mechanism	$g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$	Symbol
Chemical reaction		
First order	$-\ln(1-\alpha)$	F1
Second order	$[1/(1-\alpha)] - 1$	F2
Third order	$(1/2)([1/(1-\alpha)^2] - 1)$	F3
Diffusion		
One-way transport	α^2	D1
Two-way transport	$(1-\alpha)\ln(1-\alpha) + \alpha$	D2
Three-way transport	$[1-(1-\alpha)^{1/3}]^2$	D3
Ginstling, Brounshtein equation	$(1-2\alpha/3) - (1-\alpha)^{2/3}$	D4
Zhuravlev, Lesokhin, Tempelman equation	$[(1-\alpha)^{-1/3} - 1]^2$	D5

expression can be solved to give:

$$g(\alpha) = \frac{ART^2}{\beta E}\left(1 - \frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right). \tag{6}$$

If Eq. (6) is integrated using the Coats and Redfern method, it can be obtained:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT}. \tag{7}$$

In general, the term $2RT/E$ can be neglected since it is much less than unity for the thermal decomposition of lignocellulosic materials (Brown, 2001). Hence, plotting $\ln[g(\alpha)\,/\,T^2]$ versus $1/T$ gives a straight line with a slope $-E/R$ since $\ln(AR\,/\,\beta E)$ is almost constant. $f(\alpha)$ and $g(\alpha)$ expressions depend on the mathematical model of each conversion mechanism. If the suitable $g(\alpha)$ is applied, $\ln[g(\alpha)\,/\,T^2]$ versus $1/T$ plot is linear with high correlation coefficient (R^2) of the regression analysis. The latter allows extracting the activation energy and pre-exponential factor values.

Results and discussion

Raw material characterization

Elemental compositions as well as the "H/C" and "O/C" ratios of the different Cameroonian biomass species are listed in Table 2.

The analysis shows that elemental compositions of the different samples are in the range of typical composition values of biomass reported in literature (Cocozza et al., 2011; Wilson et al., 2011). Comparison of the different samples shows that CCs have the lowest carbon content, the highest oxygen content and therefore the highest O/C ratio. This characteristic was already observed in previous investigations (Aboyade et al., 2011). Authors found an O/C ratio ranging from 0.91 to 1.06. Such results may be attributed to the highest cellulose percentage in CC composition. In fact, it is known that the cellulose surface is rich in oxygenated groups. The typical functional groups are hydroxyl (–OH) and ether (C–O–C) (Meng et al., 2013).

In contrast, Table 2 shows that oil palm residues have the highest carbon content and the lowest oxygen content. Such behaviour was already observed in literature for PKS (Husain et al., 2002; Mahlia et al., 2001). The obtained values for carbon content were ranging from 51.5 to 52.4 (Mahlia et al., 2001; Wilson et al., 2011). This high carbon content may be attributed to the high lignin percentage in Palm Kernel Shell. In fact, the lignocellulosic analysis of the different components of PKS shows a percentage of lignin ranging from 48.2 to 53.8% (Sabil et al., 2013; Shuit et al., 2009). One may remind that lignin is rich in C═C in its aromatic ring as well as methoxyl ($-O-CH_3$) (Cocozza et al., 2011).

Concerning PMF, the high carbon content was not mentioned in literature. To our knowledge, only Wilson et al. mentioned a value of 52.2% for PMF from oil palm in Tanzania (Wilson et al., 2011). Hence, the PMF elemental composition may depend strongly on the cultivation region. Such hypothesis is confirmed by the similar hydrogen content between PMF from Cameroon and Tanzania with values close to 7% (Wilson et al., 2011). These values are higher than the hydrogen content in the PMF obtained from Malaysian plantation with values close to 6% (Mahlia et al., 2001; Sabil et al., 2013; Shuit et al., 2009; Uemura et al., 2011). Table 2 shows that PNS also has a higher carbon and oxygen content which is in agreement with literature (Arromdee and Kuprianov, 2012). This elemental composition may be attributed to the high content of cellulose and lignin in PNS. Kerr et al. noted that the chemical composition of peanut shells is 8.2% protein, 28.8% lignin, 37.0% cellulose and 2.5% hemicelluloses (Kerr et al., 1986).

The analysis of nitrogen content shows a higher value for CH. Such result was previously observed by Saenger et al. (2001). Particular attention should be given to NO_x emission during energy recovery. It is important to note that no significant sulphur contents were detected during ultimate analysis. Hence, SO_x emissions are not of concern for these samples during the combustion process.

Proximate analyses as well as the heating values were obtained for the five Cameroonian biomasses. The obtained results are shown in Table 3. Comparison between the different biomasses shows higher amounts of volatiles ranging from 66 to 84 wt.% for all species and relatively ash contents lower than 5% except for CH. High fixed carbon content for PKS is observed comparing to the other species. Such result is attributed as mentioned previously to higher lignin content. It is well known that lignin is difficult to decompose during biomass pyrolysis and its generated solid residue is very high (Yang et al., 2006). In similar way, the higher volatile matter content is observed for PMF. This observation may be attributed to a higher cellulose and hemicellulose percentage. Shuit et al. (2009) obtained PMF component composition of 34.6 and 37.5% for hemicellulose and cellulose, respectively.

The knowledge of the FC and VM contents is very important for selection of the suitable thermochemical conversion process. Hence, biomass with high volatile matter such as PMF produces high quantities of bio-oil and syngas. In contrast, biomass with high fixed carbon such as PKS is suitable for bio-char production. Moreover, the analysis of FC and VM contents offers a measure of the ease with which the biomass can be ignited and subsequently oxidised (McKendry, 2002a). Generally biomass fuels having a high fraction of volatile matter (i.e. low fixed carbon) provide a rapid gas evolution when heated, necessitating a dedicated combustor design. In contrast, biomass fuels with low volatiles must be burnt on a grate as they take a long time to burn out unless they are pulverized to a very small size. Therefore, information of FC and VM contents is essential to determine primary and secondary air supplies for the complete combustion of volatiles and biomass particles. Comparison of heating values shows that the higher energy content is obtained for PMF. Such a result is predictable since PMF has the highest volatiles and carbon contents and the lowest O/C ratio.

Thermal degradation

Figs. 1 and 2 show the TG and derivative TG (DTG) profiles for Palm Kernel Shells (PKS), Palm Mesocarp Fibre (PMF), Coffee Husk (CH), Corn Cob (CC) and Peanut Shells (PNS) under nitrogen atmosphere at a heating rate of 5 K·min^{-1}. The curves show the typical thermal degradation profile for biomasses with the three well demarked steps for moisture release, devolatilization and char formation.

Analysis of the mass loss rate (derivative thermograms) for the five samples shows a clear difference during the devolatilization step. In fact,

Table 2
Ultimate analyses of initial sample (dry basis).

Biomass	% C	% H	% O	% N	H:C ratio	O:C ratio
PKS	53.7	6.3	38.2	0.3	0.12	0.71
PMF	54.5	7.0	35.5	0.8	0.13	0.65
CH	48.3	5.6	39.5	1.6	0.12	0.82
CC	46.4	5.4	45.2	1.0	0.12	0.97
PNS	50.8	6.1	40.5	0.7	0.12	0.80

Table 3
Proximate analyses and heating values of different biomass species (as received basis).

Biomass	Moisture (%)	VM (%)	FC (%)	Ash (%)	HHV (MJ·kg^{-1})	LHV (MJ·kg^{-1})
PKS	8.2	65.6	25.0	1.2	19.5	18.0
PMF	5.7	82.0	10.2	2.1	22.7	21.0
CH	11.4	66.2	17.0	5.4	16.3	14.9
CC	8.1	77.1	12.9	1.9	16.1	14.7
PNS	7.8	77.8	12.6	1.8	18.1	16.6

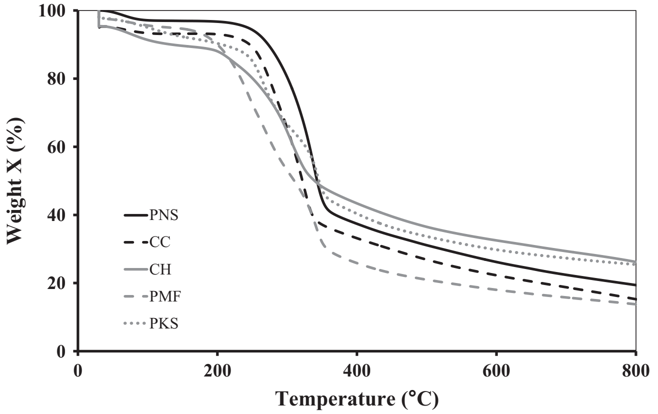

Fig. 1. TGA curves of the different samples under nitrogen atmosphere.

two distinct DTG peaks are observed during the PKS thermal degradation. The first DTG peak occurred at 261 °C with a maximum mass loss rate of 0.04% s^{-1} (0.48 wt.%·K^{-1}) is attributed to hemicellulose decomposition. The second DTG peak occurred at 343 °C with a maximum mass loss rate of 0.062%·s^{-1} (0.74 wt.%·K^{-1}) is attributed to cellulose decomposition. Orfão et al. (1999) showed that DTG peak of pure cellulose decomposition occurred at 332 °C at 0.9 wt.%·K^{-1} mass loss rate. The shifting of DTG peak to higher temperature and the decrease of the maximum loss rate for PKS are attributed to the high lignin content (~50%) comparing to cellulose (~22%) and hemicellulose (~24%) (Shuit et al., 2009). In fact, Yang et al. (2006) observed a decrease in mass loss rates of cellulose/lignin mixture with the increase in lignin content. In addition, DTG curve peak of cellulose shifting to a higher temperature was observed with increasing lignin.

The second oil palm residue, PMF, has different behaviours with three DTG peaks occurred at 242, 271 and 343 °C with maximum loss rates of 0.039% s^{-1} (0.49 wt.%·K^{-1}), 0.036% s^{-1} (0.43 wt.%·K^{-1}), and 0.051% s^{-1} (0.61 wt.%·K^{-1}), respectively. The first two peaks may be attributed to hemicellulose decomposition. In fact, PMF contains 34.6% of hemicellulose, 37.5% of cellulose and 27.9% of lignin (Shuit et al., 2009). Hemicellulose is composed from different sugars and its thermal degradation depends strongly on its characteristics. Hence, the two obtained DTG peaks may be attributed to different sugars. Stefanidis et al. (in press) have observed two peaks at 246 and 295 °C during Xylan thermal degradation under nitrogen atmosphere occurring at 0.49 and 0.75 wt.%·K^{-1}, respectively.

Fig. 2 shows also that CH and CC have different behaviours comparing to oil palm residues. In fact, both CH and CC DTG present a shoulder at lower temperatures and an outstanding point at higher temperatures. According to the previous studies in different biomass materials, the shoulder at the left hand side corresponds to the hemicellulose decomposition while the higher temperature peak in the right hand side represents the degradation of cellulose (Munir et al., 2009; Orfão et al., 1999). Comparison of CH and CC thermal degradation shows different shoulder and peak temperatures as well as different maximum loss rates. Hence, the obtained shoulder temperatures were 218 and 282 °C with a maximum mass rate of 0.013% s^{-1} (0.16 wt.%·K^{-1}) and 0.047% s^{-1} (0.56 wt.%·K^{-1}) for CH and CC, respectively. Furthermore, the peak temperatures corresponding to cellulose decomposition occurred at 307 and 328 °C with a maximum mass rate of 0.041% s^{-1} (0.49 wt.%·K^{-1}) and 0.067% s^{-1} (0.80 wt.%·K^{-1}) for CH and CC, respectively. The obtained values for CC thermal degradation are close to those found by Aboyade et al. (2011). The higher values of maximum loss rates obtained for CC may be attributed to the higher percentage of hemicellulose (46 wt.%) and cellulose (41 wt.%) in CC comparing to CH (17.8 wt.% of cellulose and 13.1wt.% of hemicellulose) (Mussatto et al., 2011). However, the lower temperatures for hemicellulose and cellulose decomposition may be attributed to higher ash contents in CH and therefore to some minerals catalytic effect such as potassium.

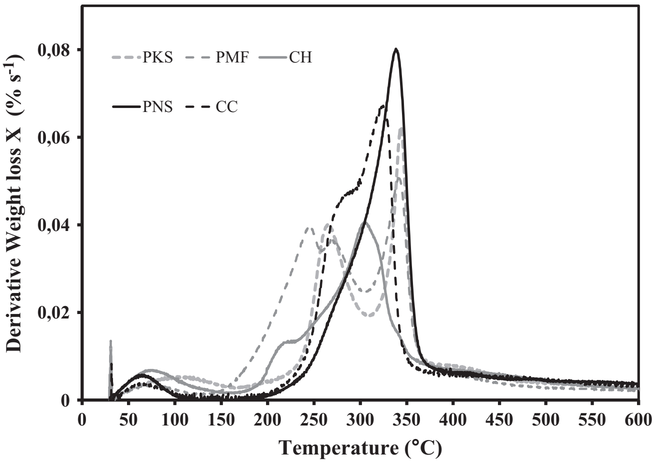

Fig. 2. DTG curves of the different samples.

The DTG curve of PNS is different from the previous biomass species. In fact, only one sharped peak is observed at 339 °C with a maximum loss rate of 0.080% s^{-1} (0.96 wt.%·K^{-1}). These values are very close to those found by Orfão et al. (1999) during the pyrolysis of pure cellulose in similar experimental condition. This result is in agreement with the PNS composition which is made of cellulose (37.0%) and lignin (28.8%) (Kerr et al., 1986).

From the obtained maximum loss rate and the corresponding temperature for the different peaks and shoulders, sample reactivities were calculated according to:

$$R_M = 100\sum\frac{R_{DTG\ max}}{T_{DTG\ max}} \tag{11}$$

where, R_M is the reactivity (% s^{-1} K^{-1}), R_{DTGmax} is the maximum weight loss rate (% s^{-1}) and T_{DTGmax} is the corresponding temperature (°C).

The obtained values are 0.45, 0.37, 0.31, 0.24 and 0.19 10^{-3}% s^{-1} K^{-1} for PMF, CC, PKS, PNS and CH respectively. These values are close to those of Elmay et al. (2012), during thermal degradation of five date palm residues (fluctuated between 0.23 and 0.40 10^{-3}% s^{-1} K^{-1}) and Munir et al. (2009) during thermal degradation of four different agricultural residues (fluctuated between 0.31 and 0.54 10^{-3}% s^{-1} K^{-1}). Comparison between the Cameroonian biomass feedstocks shows that Palm Mesocarp Fibre is promising alternative fuel with a highest reactivity.

Kinetic parameters

The TG data for the different biomasses were examined using diffusion and chemical reaction mechanisms (Table 4). Kinetic parameter analysis of the five biomass feedstocks shows that the best fit was obtained with a first order chemical reaction (F1) and diffusion mechanism (D1, D2, D3, D4) for the devolatilization region. However, the third order chemical reaction (F3) was the most reasonable for the thermal degradation during the char formation region. In literature, these kinetic models were the most suitable for describing the thermal degradation of lignocellulosic materials (Agarwal, 1985; Gil et al., 2010; Guo and Lua, 2000; Vlaev et al., 2003; Wu and Dollimore, 1998; Masnadi et al., 2014). Analysis of the kinetic models and values for the tested biomasses shows different behaviours. Hence, the devolatilization zone for PKS is divided into two stages. The first devolatilization stage, ranging from 186 to 213 °C is well described by a first order chemical reaction (F1) while D3 diffusion mechanism was effective for the second devolatilization stage in the 213–368 °C temperature range. The other diffusion mechanisms D1, D2 and D4 are also effective for describing the second devolatilization stage. Similar behaviour was observed by

Table 4
Kinetic parameters of the thermal degradation of different Cameroonian biomass species.

Sample	Temperature range	Activation energy ($kJ \cdot mol^{-1}$)	Frequency factor (s^{-1})	R^2	Function $f(\alpha)$
PKS	186–213 °C	2.7	3.0×10^{-5}	0.9806	F1
	213–368 °C	58.9	36.3	0.9805	D2
		64.6	33.0	0.9845	D3
		60.8	13.3	0.9821	D4
		77.1	884	0.9868	D5
	368–800 °C	4.2	7.6×10^{-4}	0.9953	F2
		23.5	0.49	0.9908	F3
PMF	160–377 °C	28.7	0.41	0.9885	F1
		56.8	34.2	0.9885	D2
		61.2	26.1	0.9873	D3
		57.9	9.6	0.9827	D4
		72.1	530	0.9947	D5
	377–800 °C	11.8	0.046	0.9885	F3
CH	190–356 °C	41.8	2.61	0.9882	D1
		45.3	2.18	0.9866	D2
		49.2	1.16	0.9843	D3
		46.6	0.56	0.9859	D4
		57.6	11.6	0.9784	D5
	356–800 °C	8.9	7.7×10^{-3}	0.9849	F3
CC	215–352 °C	47.8	14.0	0.9803	F1
		86.7	2.1×10^{4}	0.9819	D1
		92.0	4.3×10^{4}	0.9829	D2
		98.1	4.4×10^{4}	0.9833	D3
		94.0	1.6×10^{4}	0.9832	D4
		111.2	1.1×10^{6}	0.9819	D5
	352–752 °C	8.6	8.5×10^{-3}	0.9820	F3
PNS	208–375 °C	54.4	38.8	0.9816	F1
		97.7	1.1×10^{5}	0.9818	D1
		102.5	1.7×10^{5}	0.9808	D2
		109.0	1.8×10^{5}	0.9808	D3
		105.3	7.6×10^{4}	0.9821	D4
		117.9	3.1×10^{6}	0.9755	D5
	375–665 °C	10.5	0.014	0.9810	F3

Gil et al. (2010) who noted also two devolatilization stages during their study of the thermal behaviour and kinetics of pine and pine/coal blend. Devolatilization steps for PMF, CC and PNS were described only in one stage by both order chemical reaction (F1) and diffusion mechanism (D1, D2, D3, D4). The temperature ranges were 160–377 °C, 215–375 °C and 215–375 °C for PMF, CC and PNS, respectively. In contrast, only diffusion mechanism models are effective for the thermal degradation of CH. These obtained results are in agreement with those found in literature. In fact, diffusion mechanism models are the most effective for describing the thermal degradation of lignocellulosic materials (Agarwal, 1985). Wu and Dollimore (1998) performed kinetic studies of thermal degradation of various wood species. They showed that three-dimensional diffusion mechanism D3 was effective for spruce, hardmaple, basswood, red oak, and poplar pyrolysis. Guo and Lua (2000) found that D3 described well the pyrolysis of extracted oil palm fibres at low temperature. Vlaev et al. (2003) found that the D4 mechanism was effective for the thermal degradation of rice husk.

Moreover, several investigations showed that the first-order reaction (F1) could be a reasonable mechanism for describing the devolatilization step of biomass species. In particular, Yorulmaz and Atimtay (2010) found that the F1 mechanism was effective for the thermal degradation of treated wood such as MDF, plywood and particleboard. Wu and Dollimore (1998) showed that chemical reaction F1 was effective for softmaple pyrolysis. However, the activation energy for the tested samples is very low compared to those generally found in literature for biomass pyrolysis. Hence, the chemical reaction F1 mechanism could not be selected as an effective mechanism of these types of tropical biomass.

For the thermal degradation under inert atmosphere at the highest temperature which corresponds to lignin degradation and char formation, Table 4 shows that the third order chemical reaction (F3) mechanism was effective for this step. This third reaction order was already obtained for lignin degradation during beech pyrolysis (Anca-Couce et al, 2014) and for tropical wood biomass such as Teak and Obodo (Oluoti et al, 2014). In addition, a reaction order of 3.25 was also obtained during the second stage of spruce glucomannan and commercial konjac glucomannan pyrolysis (Moriana et al, 2014). The analysis of the kinetic parameters shows that the main values for activation energies during the devolatilization step described by the diffusion mechanism (D2, D3, D4, D5) were 45.7, 58.6, 65.4, 94.7 and 105.9 $kJ \cdot mol^{-1}$ for CH, PMF, PKS, CC and PNS, respectively. These values are in the agreement with the values obtained for the thermal degradation of hemicellulose, cellulose and lignin under inert atmosphere. Hence, samples with the highest cellulose contents (CC and PNS) have the highest activation energy values. It is well known that cellulose has the highest E_a during thermal degradation comparing to hemicellulose and lignin.

For the char formation step considering the third order chemical reaction (F3) as the effective mechanism, the obtained values were 8.6, 8.9, 10.5, 11.8 and 23.8 $kJ \cdot mol^{-1}$ for CC, CH, PNS, PMF and PKS, respectively. The lowest E_a values are in agreement with those found for char formation.

Conclusion

Thermochemical conversion of five types of Cameroonian biomass, Palm Kernel Shells (PKS), Palm Mesocarp Fibre (PMF), Coffee Husk (CH), Corn Cob (CC) and Peanut Shell (PNS), was examined using thermogravimetric analysis under nitrogen atmosphere. Decomposition TG and DTG data were used to determine devolatilization kinetic parameters by applying diffusional and chemical reaction kinetic models.

Results show that the thermal degradation of Cameroonian biomass under nitrogen atmosphere could be represented by two successive steps. A first step corresponds to a devolatilization stage characterized by high weight loss which is well described by diffusional models. Activation energies for transport diffusion mechanism ranged from 45 to 106 $kJ \cdot mol^{-1}$. The second step corresponds to char formation characterized by low weight loss rate is well described by third order chemical reaction models. Activation energies ranged from 8 to 23 $kJ \cdot mol^{-1}$. These kinetic parameters may help the development of the conversion of these abundant biomasses into energy. In fact, the obtained values from the kinetic study are useful for the configuration and the designing of the suitable reactor.

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